

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
28 September 2006 (28.09.2006)

PCT

(10) International Publication Number
WO 2006/102672 A1

(51) International Patent Classification:

C08F 259/00 (2006.01) **H01M 8/10** (2006.01)
B01D 71/28 (2006.01) **C08J 5/22** (2006.01)

(21) International Application Number:

PCT/US2006/011180

(22) International Filing Date: 24 March 2006 (24.03.2006)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:

60/665,071 24 March 2005 (24.03.2005) US

(71) Applicants (for all designated States except US): **E. I. DU PONT DE NEMOURS AND COMPANY** [US/US]; 1007 Market Street, Wilmington, DE 19898 (US). **PAUL SCHERRER INSTITUT PSI** [CH/CH]; CH-5232 Villigen PSI (CH).

(72) Inventors; and

(75) Inventors/Applicants (for US only): **ROELOFS, Mark, Gerrit** [US/US]; 514 Hemlock Drive, Hockessin, DE

19707 (US). **YANG, Zhen-Yu** [US/US]; 177 Thompson Drive, Hockessin, DE 19707 (US). **GUERSEL, Selmiye, Alkan** [TR/CH]; Seidenstrasse 12, CH-5200 Brugg (CH). **SCHERER, Guenther, Georg Anton** [DE/CH]; Talackerstrasse 9b, CH-5607 Haegglingen (CH).

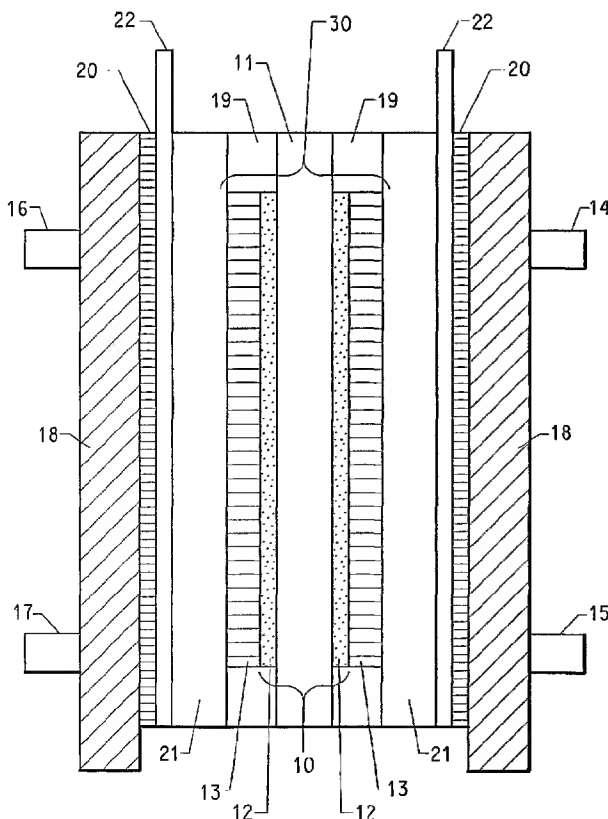
(74) Agent: **ORMAN, Thomas, W.**; E. I. du Pont de Nemours and Company, Legal Patent Records Center, 4417 Lancaster Pike, Wilmington, DE 19805 (US).

(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, LY, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NG, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SM, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH,

[Continued on next page]

(54) Title: PROCESS TO PREPARE STABLE TRIFLUOROSTYRENE CONTAINING COMPOUNDS GRAFTED TO BASE POLYMERS USING AN ALCOHOL/WATER MIXTURE



(57) Abstract: A fluorinated ion exchange polymer is prepared by grafting at least one grafting monomer derived from trifluorostyrene on to at least one base polymer in a water/alcohol mixture. These ion exchange polymers are useful in preparing catalyst coated membranes and membrane electrode assemblies used in fuel cells.



GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LT, LU, LV, MC, NL, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

— with international search report

— before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

TITLE

PROCESS TO PREPARE STABLE TRIFLUOROSTYRENE CONTAINING
COMPOUNDS GRAFTED TO BASE POLYMERS USING AN
ALCOHOL/WATER MIXTURE

5

FIELD OF THE INVENTION

The present invention relates to a novel compound grafted to a
base polymer, and its use in electrochemical cells as membranes, and
more particularly to the use of these grafted polymers in fuel cells. This
invention was made with government support under Contract No. DE-
10 FC04-02AL67606 awarded by the U.S. Department of Energy. The
government has certain rights in the invention.

BACKGROUND OF THE INVENTION

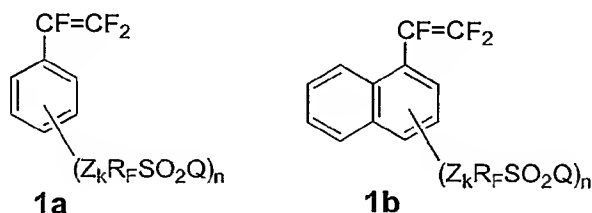
Electrochemical cells, such as fuel cells and lithium-ion batteries
are known. Depending on the operating conditions, each type of cell
15 places a particular set of requirements upon the electrolytes used in them.
For fuel cells, this is typically dictated by the type of fuel, such as hydrogen
or methanol, used to power the cell and the composition of the membrane
used to separate the electrodes. Proton-exchange membrane fuel cells,
powered by hydrogen as the fuel, could be run at higher operating
20 temperatures than currently employed to take advantage of lower purity
feed streams, improved electrode kinetics, better heat transfer from the
fuel cell stack to improve its cooling. Waste heat is also employed in a
useful fashion. However, if current fuel cells are to be operated at greater
than 100 °C then they must be pressurized to maintain adequate hydration
25 of typical proton-exchange membranes to support useful levels of proton
conductivity.

There is an ongoing need to discover novel grafted films that
improve the performance of the latest generation of electrochemical cells,
such as fuel cells and lithium-ion batteries, to develop new membrane
30 materials that will maintain adequate proton conductivity at lower levels of
hydration and have sufficient durability for the intended application.

SUMMARY OF THE INVENTION

In a first aspect, the invention provides a grafting process for making a fluorinated ion exchange polymer membrane comprising:

- (a) forming a monomer composition comprising at least one grafting monomer, in a water and alcohol mixture, wherein the grafting monomer comprises one or more of 1a and 1b:



- wherein Z comprises O, S, SO₂, or POR wherein R comprises a linear or branched perfluoroalkyl group of 1 to 14 carbon atoms optionally containing oxygen or chlorine, an alkyl group of 1 to 8 carbon atoms, an aryl group of 6 to 12 carbon atoms or a substituted aryl group of 6 to 12 carbon atoms;

- R_F comprises a linear or branched perfluoroalkylene group of 1 to 20 carbon atoms, optionally containing oxygen or chlorine;

Q is chosen from F, -OM, -NH₂, -N(M)SO₂R²_F, and -C(M)(SO₂R²_F)₂, wherein M comprises H, an alkali cation, or ammonium;

- R²_F groups comprise alkyl of 1 to 14 carbon atoms which may optionally include ether oxygens or aryl of 6 to 12 carbon atoms where the alkyl or aryl groups may be perfluorinated or partially fluorinated; and k is 0 or 1, n is 1 or 2 for formulae 1a, and n is 1, 2, or 3 for formulae 1b;

- (b) irradiating at least one base polymer with ionizing radiation, and
- (c) contacting at least one base polymer with the monomer composition from step (a), at a temperature of about 0 °C to about 120 °C for about 0.1 hours to about 500 hours.

A second aspect of the invention is a polymer made by the process described above.

A third aspect of the invention is a catalyst coated membrane comprising a polymer electrolyte membrane having a first surface and a second surface, wherein the polymer electrolyte membrane comprises the polymer described above.

5 A fourth aspect of the invention is a membrane electrode assembly comprising a polymer electrolyte membrane, having a first surface and a second surface, wherein the polymer electrolyte membrane comprises the polymer described above.

10 A fifth aspect of the invention is an electrochemical cell comprising a membrane electrode assembly, wherein the membrane electrode assembly comprises a polymer electrolyte membrane, having a first surface and a second surface, wherein the polymer electrolyte membrane comprises the polymer described above. The electrochemical cell can be a fuel cell.

15 BRIEF DESCRIPTION OF DRAWINGS

Figure 1 is a schematic illustration of a single cell assembly.

DETAILED DESCRIPTION OF THE INVENTION

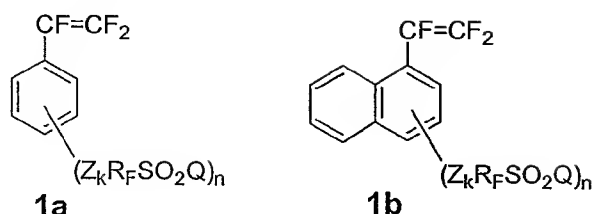
Fluorinated Ion Exchange Polymer:

20 The fluorinated ion exchange polymers of the invention are useful as polymer electrolyte membranes in fuel cells, chloralkali cells, batteries, electrolysis cells, ion exchange membranes, sensors, electrochemical capacitors, and modified electrodes.

Processes for making grafted polymers and membranes:

25 The invention is directed to a grafting process for making a fluorinated ion exchange polymer membrane comprising:

- (a) forming a monomer composition comprising at least one grafting monomer, in a water and alcohol mixture, wherein the grafting monomer comprises one or more of 1a and 1b:



wherein Z comprises O, S, SO₂, or POR wherein R comprises a linear or branched perfluoroalkyl group of 1 to 14 carbon atoms optionally

- 5 containing oxygen or chlorine, an alkyl group of 1 to 8 carbon atoms, an aryl group of 6 to 12 carbon atoms or a substituted aryl group of 6 to 12 carbon atoms;

R_F comprises a linear or branched perfluoroalkylene group of 1 to 20 carbon atoms, optionally containing oxygen or chlorine;

- 10 Q is chosen from F, -OM, -NH₂, -N(M)SO₂R²_F, and -C(M)(SO₂R²_F)₂, wherein M comprises H, an alkali cation, or ammonium;

R²_F groups comprise alkyl of 1 to 14 carbon atoms which may optionally include ether oxygens or aryl of 6 to 12 carbon atoms where the alkyl or aryl groups may be perfluorinated or partially fluorinated; and

- 15 k is 0 or 1, n is 1 or 2 for 1a, and n is 1, 2, or 3 for 1b;

(b) irradiating at least one base polymer with ionizing radiation, and

(c) contacting at least one base polymer with the monomer composition from step (a), at a temperature of about 0 °C to about 120 °C for about 0.1 hours to about 500 hours.

20

The attached pendant group(s) in Formulae 1a and 1b can be attached to any open valence in the ring. In Formula 1b the pendant group can be attached to either ring in the structure, and if more than one pendant group is present, can be attached to one or both rings.

- 25 In different embodiments of the invention, Q is F, R_F is chosen from (CF₂)_q wherein q=1 to 16, (CF₂)_qOCF₂CF₂ wherein q = 1 to 12, and (CF₂CF(CF₃)O)_qCF₂CF₂ where q is 1 to 6, and R²_F is chosen from

methyl, ethyl, propyl, butyl, and phenyl, each of which may be partially fluorinated or perfluorinated, or R_F is chosen from $(CF_2)_q$ wherein $q=1$ to 4 , $(CF_2)_qOCF_2CF_2$ wherein $q = 1$ to 4 , and $(CF_2CF(CF_3)O)_qCF_2CF_2$ where q is 1 to 2 , and R_F^2 is chosen from

5 perfluoromethyl, perfluoroethyl, and perfluorophenyl.

In the above process steps (b) and (c) can be performed simultaneously or sequentially.

The monomers can be obtained commercially or prepared using any process known in the art. Methods to prepare these monomers are

10 detailed in WO2005/113621, WO2005/049204, WO2005/113491, and WO2005/003083, all herein incorporated entirely by reference.

Base Polymer:

The base polymer to be used as the substrate for the grafting reaction may be a homopolymer or copolymer of non-fluorinated,

15 fluorinated, and perfluorinated monomers. Partially or completely fluorinated polymers often impart increased chemical stability and are more typical. The base polymer is typically chosen so that it imparts desirable mechanical properties to the final grafted polymer, is stable to the irradiation used to activate the polymer for grafting, and is stable under

20 the conditions to which it is exposed during use. For separators or membranes it is desirable that the base polymer be present in the form of a film, though other shapes may be desired depending on the electrochemical use. Some typical base polymers may include poly(ethylene-tetrafluoroethylene-termonomer (ETFE) that comprises a

25 terpolymer of ethylene and tetrafluoroethylene (TFE), in the range of 35:65 to 65:35 (mole ratios) with from 1 to 10 mole% of a termonomer, perfluorobutyl ethylene in the case of DuPont Tefzel®; ETFE copolymers also using other termonomers (Neoflon® ETFE); ECTFE that comprises a copolymer of ethylene and chlorotrifluoroethylene; FEP that comprises a

30 copolymer of TFE and hexafluoropropylene (HFP), optionally containing a minor amount (1-3 mol%) of perfluoro(alkyl vinyl ether) (PAVE), usually perfluoro(propyl vinyl ether) (PPVE) or perfluoro(ethyl vinyl ether) (PEVE); PFA that comprises a copolymer of TFE and PAVE, wherein PAVE may

be PPVE or PEVE; MFA that comprises a copolymer of TFE, PMVE, and PPVE; PTFE that comprises a homopolymer of TFE; modified PTFE, that contains up to 0.5 mol% of another monomer, usually a PAVE; PVF that comprises a polymer of vinyl fluoride (VF); PVDF that comprises a polymer of vinylidene fluoride (VF₂); copolymers of VF₂ and HFP which are sold under the trademarks KynarFlex® and Viton® A by Atofina and by DuPont, respectively; polyethylene and polypropylene. The term "modified" distinguishes these polymers from copolymers of TFE. The modified PTFE polymers are, like PTFE, not melt processible.

Typically, the base polymer may be chosen from poly(ethylene-tetrafluoroethylene), poly(ethylene-tetrafluoroethylene-termonomer) (Tefzel®, Neoflon® ETFE); poly(tetrafluoroethylene-hexafluoropropylene) (Teflon® FEP); poly(tetrafluoroethylene-perfluorovinylether) (Teflon® PFA), polytetrafluoroethylene (Teflon® PTFE); poly(ethylene-chlorotrifluoroethylene); poly(vinylidene fluoride) (Kynar® or Solef®); and poly(vinylidene fluoride-hexafluoropropylene) (Kynar® Flex). More typically, the base polymer is chosen from poly(ethylene-tetrafluoroethylene-termonomer), poly(tetrafluoroethylene-hexafluoropropylene), poly(tetrafluoroethylene-perfluoropropylvinylether), and poly(vinylidene fluoride).

Free radicals may be created in the base polymer in order to produce attachment sites for the grafting monomers using radiation. When the base polymer is in film form, the films are known as irradiated films. The radiation dosage should be sufficient to allow for the desired graft level to be reached, but not so high as to cause excessive radiation damage. Graft level is defined as (wt. of grafted polymer – wt. of base polymer)/(wt. of base polymer). (This is also known as weight uptake). The ionizing radiation may be provided in the form of electron beam, gamma ray, or X-rays. Electron beam irradiation is typically performed at a high dose rate that may be advantageous for commercial production. The irradiation may be done while the base polymer is in contact with the grafting monomers (simultaneous irradiation and grafting). However, if the free radicals of the base polymer are sufficiently stable, then the irradiation

may be performed first and in a subsequent step the base polymer may be brought into contact with the grafting monomers (post-irradiation grafting). Base polymers suitable for the post-irradiation grafting method are usually fluorinated polymers. In this case the irradiation may typically be done at
5 sub-ambient temperatures, for example with base polymer cooled with dry ice, and it may be stored at a sufficiently low temperature to prevent decay of the free radicals prior to its use in the grafting reaction.

With some substrates, such as poly(ethylene-tetrafluoroethylene) the irradiation may be performed in the presence of oxygen or in an
10 oxygen-free environment, and an appreciable graft level can be obtained in either case. Typically grafting may be performed in an inert gas, such as nitrogen or argon. This may be accomplished by loading the base polymer films, within an inert-atmosphere box, into oxygen-barrier bags, sealing them shut (with or without grafting monomers and solvent), and
15 then irradiating. In the case of post-irradiation grafting, the base polymer may then also be stored in the oxygen-free environment before and during the grafting reaction.

The grafting reaction may be performed by exposing the base polymer to a monomer composition containing the grafting monomers. It is
20 generally desirable to lower the quantity of fluorinated monomer used in the grafting reaction, and this may be accomplished by using a larger volume of a grafting liquid in which some of the monomer is dispersed. The monomer composition is thus a mixture of alcohols, water, and the grafting monomers. Suitable alcohols include aliphatic alcohols that are
25 optionally partially fluorinated and optionally containing ether linkages, and can include glycols. The alcohol is typically a C1 to C12 alcohol. Typical alcohols include n-propanol, isopropanol, butanol, ethanol, methanol, $R''(OCH_2CH_2)_pOH$, where R'' is methyl, ethyl, and p is 1-6. The mixture can comprise 0.1 to 80 volume % alcohol, typically 10-60%. The optimized
30 ratio will depend on the choice of monomer. Although some of the monomer may additionally present as a separate monomer-rich phase, the monomer needs to be at least partially dissolved in the water/alcohol

mixture. The alcohol also needs to be at least partially soluble in the water.

The alcohol and water mixture can optionally contain one or more surfactants. The surfactant can be anionic, cationic, or nonionic, and can be fluorinated. Suitable surfactants include, are not limited to, sodium dodecylsulfate, alkyl benzene sulfonates, dextrans, alkyl-ether sulfonates, ammonium sulfates, Triton® surfactants, and fluorinated surfactants such as C8 (ammonium perfluorooctanoate), Zonyl® fluorosurfactants such as Zonyl® 62, Zonyl® TBS, Zonyl® FSP, Zonyl® FS-62, Zonyl® FSA, Zonyl® FSH, and fluorinated alkyl ammonium salts such as but not limited to $R'_wNH_{(4-w)}X$ wherein X is Cl^- , Br^- , I^- , F^- , HSO_4^- , or $H_2PO_4^-$, where R' is $(R_FCH_2CH_2)-$. Zonyl® fluorosurfactants are available from E. I. DuPont de Nemours, Wilmington, DE. and in general are anionic, cationic, amphoteric or nonionic oligomeric hydrocarbons containing ether linkages and fluorinated substituents. For example, Zonyl® FSP is an anionic surfactant of the formula $(R_FCH_2CH_2)_xPO(O-NH_4^+)_y$, where $x + y = 3$ and Zonyl® FSH is a nonionic surfactant of the formula $R_FCH_2CH_2O(CH_2CH_2O)_wH$.

Enhancing additives can optionally be used to enhance the grafting rate or to enhance film quality. Suitable additives are water insoluble organic compounds that are solvents for the monomer or monomers used. One or more enhancing additives may be used. The enhancing additive is typically present at an amount of 0.5 to 300 weight % of the monomer. Suitable enhancing additives can include α,α,α -trifluorotoluene, dichlorobenzotrifluoride, chlorobenzotrifluoride, chlorobenzene, dichlorobenzene, trichlorobenzene, fluorobenzene, difluorobenzene, trifluorobenzene, perfluorobenzene, toluene, p-xylene, m-xylene, o-xylene, or C5-C10 aliphatic hydrocarbon, fluorohydrocarbon, fluorocarbon, and fluoroether.

Grafting may be accomplished by contacting the base polymer films, during irradiation or subsequent to irradiation, with the monomer composition and holding films at about 0 °C to about 120 °C for about 0.1 to about 500 hours. Typical temperatures are about 25 °C to about 100

°C, more typically about 35 to about 90 °C, and most typically about 40 to about 80 °C. Typical times are about 10 min to about 300 hours, more typically about 1 hour to about 200 hours, and most typically about 1 hour to about 100 hours. During grafting the monomer composition may be
5 agitated, for example by stirring, shaking, or pumping. This agitation may serve to replace monomer-depleted solution near the surface of the film, or for cases where the monomer forms a separate phase, to replenish the monomer in the alcohol/water phase. Subsequent to the grafting reaction, the alcohol, water, surfactants and additives, if present and unreacted
10 monomer may be removed by extraction with a low-boiling solvent or through vaporization. The grafted polymer may also be extracted with a solvent in order to remove any polymer formed in the film that is not grafted to the base film.

Preparation of Ionic Polymers:

15 This invention provides for the facile conversion of the fluorosulfonyl fluorides to acid form, without the use of sulfonation reagents. Polymers grafted with the monomers bearing pendant sulfonyl fluoride groups may be hydrolyzed with bases such as MOH or M_2CO_3 ($M = Li, Na, K, Cs, NH_4$) or MOH in MeOH and/or DMSO, and water. The hydrolysis may
20 usually be carried out at room temperature to about 100°C, typically at room temperature to about 80°C. With polymeric substrates such as PVDF that are sensitive to strong base, it is preferable to use the weaker carbonate bases that avoid decomposition of the substrate. Treatment of polymeric salts with acids such as HNO_3 gives polymeric acids.

25 The grafted sulfide polymers ($Z = S$) may be oxidized to sulfone polymers ($Z = SO_2$) using CrO_3 or hydrogen peroxide.

Electrochemical Cell:

As shown in Figure 1, an electrochemical cell, such as a fuel cell, comprises a catalyst-coated membrane (CCM) (10) in combination with at
30 least one gas diffusion backing (GDB) (13) to form an unconsolidated membrane electrode assembly (MEA). The catalyst-coated membrane (10) comprises a polymer electrolyte membrane (11) discussed above and catalyst layers or electrodes (12) formed from an electrocatalyst coating

composition. The fuel cell may be further provided with an inlet (14) for fuel, such as hydrogen; liquid or gaseous alcohols, e.g. methanol and ethanol; or ethers, e.g. diethyl ether, etc., an anode outlet (15), a cathode gas inlet (16), a cathode gas outlet (17), aluminum end blocks (18) tied
5 together with tie rods (not shown), a gasket for sealing (19), an electrically insulating layer (20), graphite or metal current collector blocks with flow fields for gas distribution (21), and gold plated current collectors (22).

Alternately, gas diffusion electrodes comprising a gas diffusion backing having a layer of an electrocatalyst coating composition thereon
10 may be brought into contact with a solid polymer electrolyte membrane to form the MEA.

The electrocatalyst coating compositions used to apply the catalyst layers as electrodes on the CCM (10) or the GDE comprise a combination of catalysts and binders dispersed in suitable solvents for the binders, and
15 may include other materials to improve electrical conductivity, adhesion, and durability. The catalysts may be unsupported or supported, typically on carbon, and may differ in composition depending on their use as anodes or cathodes. The binders may consist of the same polymer used to form the polymer electrolyte membrane (11), but may contain in part or
20 be solely composed of other suitable polymer electrolytes as needed to improve the operation of the fuel cell. Some examples include Nafion® perfluorosulfonic acid, sulfonated polyether sulfones.

The fuel cell utilizes a fuel source that may be in the gas or liquid phase, and may comprise hydrogen, an alcohol, or an ether. The fuel is
25 humidified to the degree required to maintain adequate ionic conductivity in the solid polymer electrolyte membrane discussed above so that the fuel cell provides a high power output. Depending on the operating temperature, the fuel cell may be operated at elevated pressures to maintain the required degree of humidification. Typically a gaseous
30 humidified hydrogen feed or methanol/water solution may be supplied to the anode compartment, and air or oxygen supplied to the cathode compartment.

Catalyst Coated Membrane:

A variety of techniques are known for CCM manufacture, which apply an electrocatalyst coating composition similar to that described above onto a solid polymer electrolyte membrane. Some known methods
5 include spraying, painting, patch coating and screen, decal, pad or flexographic printing.

In one embodiment of the invention, the MEA (30), shown in Figure 1, may be prepared by thermally consolidating the gas diffusion backing (GDB) with a CCM at a temperature of under about 200 °C, typically about
10 140 to about 160 °C. The CCM may be made of any type known in the art. In this embodiment, an MEA comprises a solid polymer electrolyte (SPE) membrane with a thin catalyst-binder layer disposed thereon. The catalyst may be supported (typically on carbon) or unsupported. In one method of preparation, a catalyst film is prepared as a decal by spreading
15 the electrocatalyst coating composition on a flat release substrate such as Kapton® polyimide film (available from the DuPont Company). After the coating dries, the decal is transferred to the surface of the SPE membrane by the application of pressure and heat, followed by removal of the release substrate to form a catalyst coated membrane (CCM) with a catalyst layer
20 having a controlled thickness and catalyst distribution. Alternatively, the catalyst layer is applied directly to the membrane, such as by printing, and the catalyst film is then dried at a temperature not greater than about 200 °C.

The CCM, thus formed, is then combined with a GDB to form the
25 MEA (30). The MEA is formed, by layering the CCM and the GDB, followed by consolidating the entire structure in a single step by heating to a temperature no greater than about 200 °C, typically in the range of about 140 to about 160 °C, and applying pressure. Both sides of the MEA can be formed in the same manner and simultaneously. Also, the composition of
30 the catalyst layer and GDB may be different on opposite sides of the membrane.

The invention is illustrated in the following examples.

EXAMPLES

Example 1: Irradiated Films

ETFE films were obtained in thicknesses of 30 μm and 55 μm (Tefzel® LZ5100 and LZ5200, DuPont Company, Wilmington, DE). PVdF
5 films were obtained with a thickness 50 μm (Kynar® Goodfellow Corp, Berwyn, PA). The films were degassed and brought into a nitrogen-filled glove box. They were cut to size and sealed inside gas-barrier bags (PPD aluminum-foil-barrier bags from Shield Pack, Inc., West Monroe, LA). Dry ice pellets were placed in a metal tray for cooling and the bags with films
10 were placed into the metal tray. The films were irradiated using an electron beam accelerator using 1 MV and a current of 2.2 mA or 4.5 MV and 25 mA. Up to 6 films were placed in each bag, and the bags were stacked up to 2 high in the tray. The beam was electronically scanned across a 40" aperture while the metal tray was moved slowly beneath the
15 beam. Each pass resulted in a dosage of 20 kGy, and from 1 to 13 passes were used resulting in total dosages between 20 and 260 kGy. For dosages above 190 kGy, the passes were broken in to two groups with the inclusion of a three-minute pause between the groups to allow the bags to cool. The irradiated films were stored in the bags under dry ice or
20 in a refrigerator cooled to $-40\text{ }^{\circ}\text{C}$.

Example 2

Tefzel® films from Example 1 of 27 μm thickness and irradiated to 140 kGy were brought into a nitrogen-purged glove box. Into a 30-ml jar was placed 4.82 g n-propanol, 13.2 g water, and 1.4 g of monomer
25 $p\text{-CF}_2=\text{CF-C}_6\text{H}_4\text{-S}(\text{CF}_2)_2\text{SO}_2\text{F}$ (para isomer). The mixture was sonicated for 5 min using a 200 W 40 kHz ultrasonic generator (Dukane 40TP200). This dispersed the monomer into the alcohol/water liquid mixture, though some of the monomer separated out as a separate liquid phase, especially later as it was heated. These liquids were deoxygenated by bubbling with
30 nitrogen and brought into the glove box. The Tefzel® film was cut to size and weighed 195 mg. The film and liquids were placed in a 20-ml vial equipped with a magnetically-driven stir bar rotating at 500 rpm, the vial

sealed with a septum, and the vial was heated at 70 °C for 70 hr. The film was removed from the vial, rinsed with n-propanol, extracted in tetrahydrofuran (THF) at 60 °C for 4 hr, dried, and reweighed to give 273 mg or 40% graft level (GL, % weight uptake).

5 Example 3

Tefzel® films from Example 1 of 27 µm thickness and irradiated to 140 kGy were brought into a nitrogen-purged glove box, cut to 25 mm X 50 mm, and weighed. Into each of ten 8-oz rectangular glass bottles was placed 0.50 g of deoxygenated monomer $p\text{-CF}_2=\text{CF-C}_6\text{H}_4\text{-S}(\text{CF}_2)_2\text{SO}_2\text{F}$,
10 one film, water Liquid A, alcohol Liquid B, and optional additive α,α,α -trifluorotoluene (TFT, Liquid C), the Liquids indicated with their weight in the Table below. A piece of Teflon® mesh was added to each bottle, the bottles were sealed with their caps, and placed on their sides with the mesh on top of the Tefzel® film. The bottles were placed in an
15 incubator shaker box (New Brunswick Scientific Co., Inc. Series 25) heated to 60 °C and gently shaken at 125 rpm for 96 hr. After this grafting reaction, the liquids were poured out of the bottles and approximately 70 ml of THF was added to each bottle. The grafted films were extracted using the tetrahydrofuran for 18 hr at ambient temperature,
20 after which the films were removed, dried in ambient air, reweighed, and their size remeasured with the results indicated in the Table below. The relative level of wrinkles from more/rougher to less/smooth was judged to be

$D > A > E, B, H > G, J > F, C > I$

25

Sample	Liq A	Wt A (g)	Liq B	Wt B (g)	Liq C	Wt C (g)	GL (%)	dim mm ²	thick (μm)
A	water	8.0	methanol	2.0			91	25X70	36
B	water	5.0	methanol	5.0			56	35X80	30
C	water	2.0	methanol	8.0			84	30X80	36
D	water	8.0	ethanol	2.0			174	35X67	49
E	water	5.0	ethanol	5.0			172	37X60	42
F	water	2.0	ethanol	8.0			36	25X50	28
G	water	5.0	ethanol	5.0	TFT	0.05	192	40X60	41
H	water	8.0	n-propanol	2.0			198	25X60	47
I	water	2.0	butanol	8.0			0	25X55	24
J	water	9.0	butanol	1.0	TFT	0.05	165	25X60	34

Example 4

To a small glass jar in a nitrogen-purged glove box was added 8.00 g n-propanol, 3.53 g water, 0.97 g of a 20 wt% aqueous solution of C8 (enhancement additive), and 1.77 g monomer $p\text{-CF}_2=\text{CF-C}_6\text{H}_4\text{-S}(\text{CF}_2)_2\text{SO}_2\text{F}$. The liquids were sonicated for 5 minutes, sealed with a septum, deoxygenated with nitrogen bubbling for 10 minutes, and brought into the glove box. Tefzel® film of dimension 27 μm X 100 mm X 110 mm was irradiated as in Example 1 with a dosage of 260 kGy, brought into the glove box, and weighed. The film was wrapped in Teflon® mesh, and it and the liquids were placed into a 41 mm OD glass tube and sealed. The tube was held with its axis horizontal and slowly rotated, such as to agitate the grafting liquid(s) and to repetitively immerse successive parts of the film in the grafting liquid(s), while it was heated at 61 °C for 91 hr. The film was extracted in THF at ambient temperature for 4 hr, dried, and weighed. The graft level (weight uptake) was 105% and the dimensions of the grafted film were 35 μm X 120 mm X 135 mm.

Example 5

A 30 mL bottle with a stirring bar was charged with a Tefzel® film irradiated with 140 kGy dosage under nitrogen then water, n-propyl alcohol and $p\text{-CF}_2=\text{CF-C}_6\text{H}_4\text{-S}(\text{CF}_2)_2\text{SO}_2\text{F}$ monomer in amounts as listed below table were added into the bottle under N₂. The mixture was stirred in the sealed bottle at 60°C for 3 days. The films were removed from the bottle water and dried in a vacuum oven at 60°C with nitrogen bleed for 2 hrs to give the grafted film. Graft level was calculated as $(w_g - w)/w$, where w is the

initial weight of the film and w_g is the weight of the dried washed grafted film.

Example No.	PrOH (mL)	H ₂ O (mL)	monomer (g)	GL% after drying
5a	5	20	1	66
5b	18	7	1	34.5
5c	15	10	1	177
5d	10	15	1	215

5 Example 6

Tefzel® ETFE (LZ100, LZ200, DuPont Circleville, USA) was used as the base polymer in the form of 27 or 65 μm thick films. The film was cut into pieces of 40 mm length (parallel to the extrusion direction) and 40 mm width for screening experiments or was cut to 80 X 80 mm² for the preparation of fuel cell membranes. The films were washed with ethanol and dried at 80 °C under vacuum. All films were placed in oxygen-barrier bags, repeatedly evacuated and purged with purified nitrogen to deoxygenate them, and the bags were sealed closed inside a glove box. Electron beam irradiation was performed (Studer AG, Däniken, Switzerland) to give irradiation dosages of 20 - 300 kGy (1 Gray = 1 J energy absorbed per kg). The accelerating voltage was 2.2 MV, the beam current was between 5 and 20 mA, and the dose rate was typically $15.1 \pm 1.1 \text{ kGy s}^{-1}$. For higher irradiations of 50-200 kGy, the films were placed on top of dry ice to prevent degradation of the radicals in the ETFE films via beam-induced heating. Irradiation doses were verified with radiochromic film dosimeters. The irradiated films were stored at -80 °C until they were grafted.

Tefzel® films of 25 μm thickness (8 cm x 8 cm) and irradiated to 200 kGy were brought into a nitrogen-purged glove box. Into a glass reactor was placed 32.5 mL of n-propanol, 16 mL of water and 1.5 mL of monomer $p\text{-CF}_2=\text{CF-C}_6\text{H}_4\text{O}(\text{CF}_2)_2\text{SO}_2\text{F}$. The mixture was sonicated for 5

min. Next it was deoxygenated by bubbling with nitrogen and brought into the glove box. The Tefzel[®] film was placed into the reactor at 70 °C and allowed to react for the times listed below. Graft level was calculated as $(wg-w)/w$, where w is the initial weight of the film and wg is the weight of the dried washed grafted film.

sample	reaction time(h)	GL(%)
A	38	154
B	44	225
C	48	277

Example 7

Tefzel[®] films of 25 μm thickness (8 cm x 8 cm) and irradiated to 200 kGy were brought into a nitrogen-purged glove box. Into a glass reactor was placed 30 mL of n-propanol, 18 mL of water and 2 mL of monomer $p\text{-CF}_2=\text{CF-C}_6\text{H}_4(\text{CF}_2)_2\text{O}(\text{CF}_2)_2\text{SO}_2\text{F}$. The mixture was sonicated for 5 min. Next it was deoxygenated by bubbling with nitrogen and brought into the glove box. The Tefzel[®] film was placed into the reactor at 60°C and allowed to react for the times listed below.

sample	reaction time(h)	GL(%)
A	64	116
B	72	152
C	74	162

Example 8

Tefzel[®] films of 25 μm thickness (8 cm x 8 cm) and irradiated to 200 kGy were brought into a nitrogen-purged glove box. Into a glass reactor was placed 30 mL of n-propanol, 17 mL of water and 3 mL of monomer $p\text{-CF}_2=\text{CF-C}_6\text{H}_4\text{S}(\text{CF}_2)_2\text{SO}_2\text{F}$. The mixture was sonicated for 5 min. Next it was deoxygenated by bubbling with nitrogen and brought into

the glove box. The Tefzel[®] film was placed into the reactor at 60 °C and allowed to react for the times listed below.

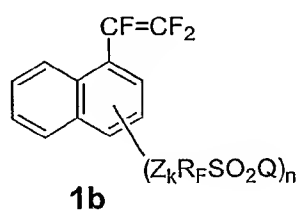
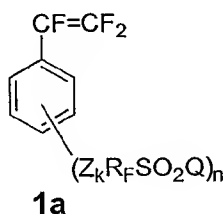
sample	reaction time(h)	GL(%)
A	72	89
B	96	109

CLAIMS

What is claimed is:

1. A grafting process for making a fluorinated ion exchange polymer membrane comprising:

- 5 (a) forming an monomer composition comprising at least one grafting monomer, in a water and alcohol mixture; wherein the grafting monomer comprises one or more of 1a and 1b:



- 10 wherein Z comprises O, S, SO₂, or POR wherein R comprises a linear or branched perfluoroalkyl group of 1 to 14 carbon atoms optionally containing oxygen or chlorine, an alkyl group of 1 to 8 carbon atoms, an aryl group of 6 to 12 carbon atoms or a substituted aryl group of 6 to 12 carbon atoms;

15 R_F comprises a linear or branched perfluoroalkylene group of 1 to 20 carbon atoms, optionally containing oxygen or chlorine;

Q is chosen from F, -OM, -NH₂, -N(M)SO₂R²_F, and -C(M)(SO₂R²_F)₂, wherein M comprises H, an alkali cation, or ammonium;

- 20 R²_F groups comprise alkyl of 1 to 14 carbon atoms which may optionally include ether oxygens or aryl of 6 to 12 carbon atoms where the alkyl or aryl groups may be perfluorinated or partially fluorinated; and

k is 0 or 1; n is 1 or 2 for **1a** and n is 1, 2, or 3 for **1b**;

- (b) irradiating at least one base polymer with ionizing radiation, and

- 25 (c) contacting at least one base polymer with the monomer composition from step (a), at a temperature of about 0 °C to about 120 °C for about 0.1 hours to about 500 hours.

2. The process of Claim 1 wherein the alcohol is a C1 to C12 aliphatic alcohol or glycol, optionally containing fluorine, and optionally containing ether linkages.

3. The process of Claim 2 wherein the alcohol is n-propanol, isopropanol, ethanol, methanol, butanol or $R''(OCH_2CH_2)_pOH$, wherein R'' is methyl or ethyl and p is 1-6.

4. The process of Claim 1 wherein the alcohol and water mixture comprises 0.1 to 80 volume percent alcohol.

5. The process of Claim 4 wherein the alcohol and water mixture comprises 10 to 60 volume percent alcohol.

6. The process of Claim 1 wherein the alcohol and water mixture optionally includes one or more enhancing additives.

7. The process of Claim 6 wherein the enhancing additive is α,α,α -trifluorotoluene, dichlorobenzotrifluoride, chlorobenzotrifluoride, chlorobenzene, dichlorobenzene, trichlorobenzene, fluorobenzene, difluorobenzene, trifluorobenzene, perfluorobenzene, toluene, p-xylene, m-xylene, o-xylene, or C5-C10 aliphatic hydrocarbon, fluorohydrocarbon, fluorocarbon, or fluoroether.

8. The process of Claim 1 wherein the enhancing additive is present at an amount of 0.5 to 300 weight percent of the monomer.

9. The process of Claim 1 wherein the at least one base polymer is in film form.

10. The process of Claim 1 wherein steps (b) and (c) are performed simultaneously.

11. The process of Claim 1 wherein steps (b) and (c) are performed sequentially.

12. The process of Claim 1 wherein Q comprises F.

13. The process of Claim 1 wherein R_F is chosen from $(CF_2)_q$ wherein $q=1$ to 16, $(CF_2)_qOCF_2CF_2$ wherein $q = 1$ to 12, and $(CF_2CF(CF_3)O)_qCF_2CF_2$ where q is 1 to 6, and R_F^2 is chosen from methyl, ethyl, propyl, butyl, and phenyl, each of which may be partially fluorinated or perfluorinated.

14. The process of Claim 13 wherein R_F is chosen from $(CF_2)_q$ wherein $q=1$ to 4, $(CF_2)_qOCF_2CF_2$ wherein $q = 1$ to 4, and $(CF_2CF(CF_3)O)_qCF_2CF_2$ where q is 1 to 2, and R_F^2 is chosen from perfluoromethyl, perfluoroethyl, and perfluorophenyl.

5 15. The process of Claim 1 wherein the grafting monomer is $p-CF_2=CF-C_6H_4(CF_2)_2O(CF_2)_2SO_2F$ or $p-CF_2=CF-C_6H_4O(CF_2)_2SO_2F$.

16. The process of Claim 1 wherein the base polymer is chosen from poly(ethylene-tetrafluoroethylene), poly(ethylene-chlorotrifluoroethylene), poly(tetrafluoroethylene-hexafluoropropylene),
 10 poly(tetrafluoroethylene-perfluoroalkyl vinyl ether), poly(tetrafluoroethylene-perfluoromethyl vinyl ether), poly(tetrafluoroethylene-perfluoropropyl vinyl ether), polytetrafluoroethylene, modified polytetrafluoroethylene, polyvinyl fluoride, polyvinylidene fluoride, poly(vinylidene fluoride-hexafluoropropylene),
 15 polyethylene, and polypropylene.

17. The process of Claim 1 wherein the base polymer comprises a partially or completely fluorinated polymer.

18. The process of Claim 17 wherein the base polymer is chosen from poly(ethylene-tetrafluoroethylene), poly(ethylene-tetrafluoroethylene-
 20 termonomer), poly(tetrafluoroethylene-hexafluoropropylene), poly(tetrafluoroethylene-perfluorovinylether), polytetrafluoroethylene, poly(ethylene-chlorotrifluoroethylene); poly(vinylidene fluoride), and poly(vinylidenefluoride-hexafluoropropylene).

19. A polymer made by the process of Claim 1.

25 20. A catalyst coated membrane comprising a polymer electrolyte membrane having a first surface and a second surface, wherein the polymer electrolyte membrane comprises the polymer of Claim 19.

21. A membrane electrode assembly comprising a polymer electrolyte membrane, having a first surface and a second surface,
 30 wherein the polymer electrolyte membrane comprises the polymer of Claim 19.

22. An electrochemical cell comprising a membrane electrode assembly, wherein the membrane electrode assembly comprises a polymer electrolyte membrane, having a first surface and a second surface, wherein the polymer electrolyte membrane comprises the polymer
5 of Claim 19.

23. The electrochemical cell of Claim 22 wherein the electrochemical cell is a fuel cell.

1/1

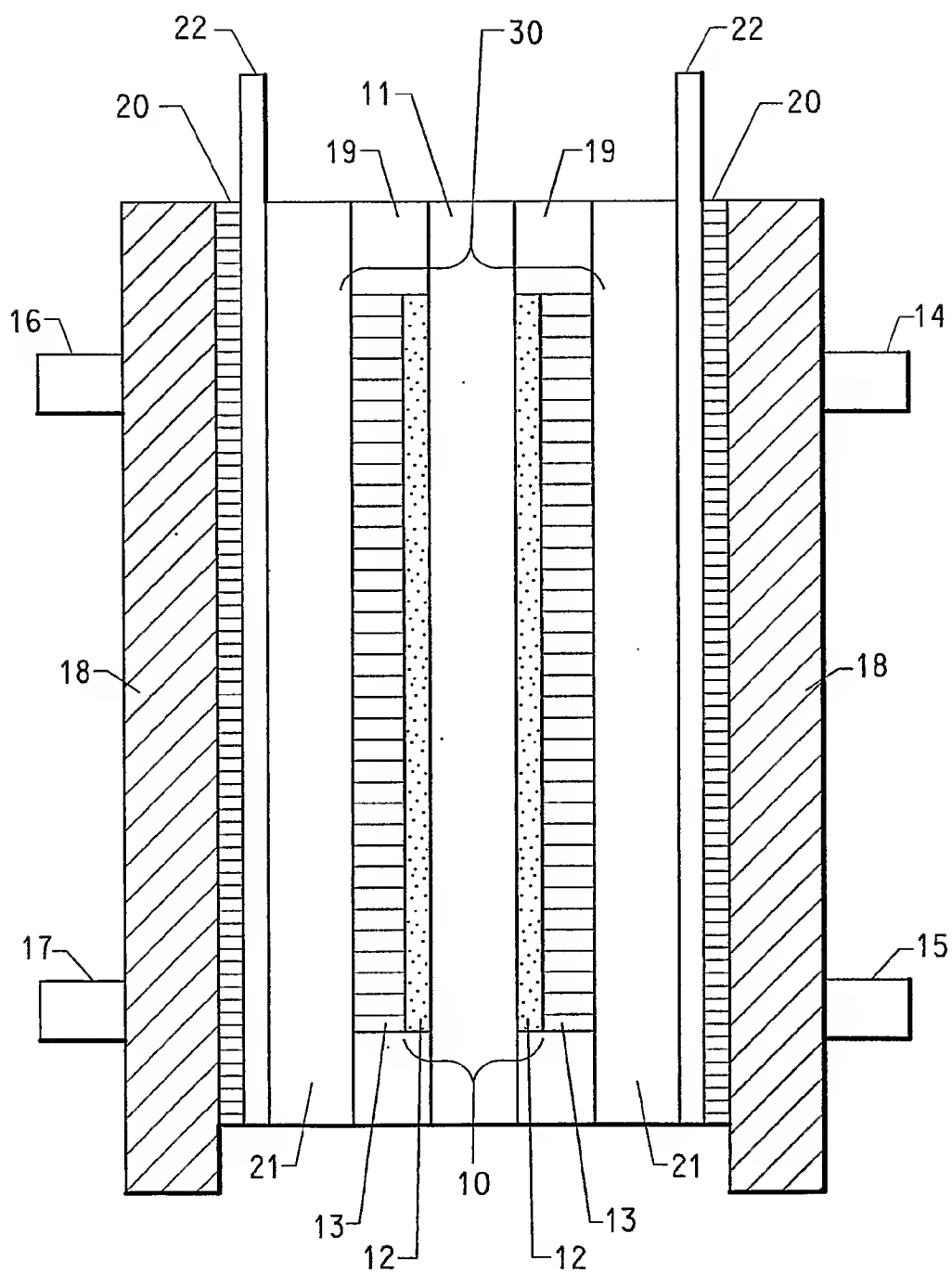


FIG. 1

INTERNATIONAL SEARCH REPORT

International application No

PCT/US2006/011180

A. CLASSIFICATION OF SUBJECT MATTER

INV. C08F259/00 B01D71/28 H01M8/10 C08J5/22

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C08F B01D H01M

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P,X	WO 2005/113621 A (E.I. DUPONT DE NEMOURS AND COMPANY; YANG, ZHEN-YU; ROELOFS, MARK, GERR) 1 December 2005 (2005-12-01) cited in the application page 13, line 11 - line 14 page 14, line 27 - line 32; claim 18	1-23
X	US 2005/049319 A1 (STONE CHARLES ET AL) 3 March 2005 (2005-03-03) examples 1,2	19-23
A	the whole document	1-18
X	US 2004/016693 A1 (STONE CHARLES) 29 January 2004 (2004-01-29) examples	19-23
A	the whole document	1-18
	----- -/--	



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents :

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

- *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- *Z* document member of the same patent family

Date of the actual completion of the international search

19 July 2006

Date of mailing of the international search report

26/07/2006

Name and mailing address of the ISA/

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Iraegui Retolaza, E

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2006/011180

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 6 359 019 B1 (STONE CHARLES ET AL) 19 March 2002 (2002-03-19) column 7, line 12 - line 19	19-23
A	the whole document -----	1-18
X	US 2002/137806 A1 (STONE CHARLES ET AL) 26 September 2002 (2002-09-26) paragraphs [0002], [0048], [0049]	19-23
A	the whole document -----	1-18

INTERNATIONAL SEARCH REPORT

information on patent family members

International application No

PCT/US2006/011180

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 2005113621	A	01-12-2005	NONE
US 2005049319	A1	03-03-2005	NONE
US 2004016693	A1	29-01-2004	NONE
US 6359019	B1	19-03-2002	AT 213006 T 15-02-2002
		AU 733804 B2	24-05-2001
		AU 1017699 A	31-05-1999
		CA 2309631 A1	20-05-1999
		WO 9924497 A1	20-05-1999
		DE 69803801 D1	21-03-2002
		DE 69803801 T2	20-06-2002
		EP 1034212 A1	13-09-2000
		JP 2001522914 T	20-11-2001
US 2002137806	A1	26-09-2002	NONE